

**THAT WHICH IS CLAIMED IS:**

1. A method of coating a microelectronic substrate, comprising the steps of:

(a) providing a microelectronic substrate in an enclosed vessel, said substrate having a surface portion;

(b) at least partially filling said enclosed vessel with a first supercritical fluid so that said first supercritical fluid contacts said surface portion, said first supercritical fluid carrying a coating component; then

(c) adding a separate compressed gas atmosphere to said reaction vessel so that a boundary is formed between said first supercritical fluid and said separate compressed gas atmosphere, said second compressed gas atmosphere having a density less than said first supercritical fluid; and then

(d) displacing said first supercritical fluid from said vessel by continuing adding said separate compressed gas atmosphere to said vessel so that said boundary moves across said surface portion and a thin film of coating component is deposited on said microelectronic substrate.

2. The method of claim 1, wherein said first supercritical fluid dissolves or disperses into said separate compressed gas atmosphere during said displacing step while said thin film of coating component is deposited.

3. The method of claim 1, further comprising the step of:

at least partially filling said enclosed vessel with a secondary compressed gas between said providing step (a) and said at least partially filling step (b).

4. A method according to claim 1, wherein said first supercritical fluid and said second compressed gas atmosphere are in said vessel are at a pressure of between about 1,000 and 10,000 psi and a temperature of between about 30 and 250 degrees Centigrade.

5. A method according to claim 1, wherein:

said first supercritical fluid comprises carbon dioxide;

said separate compressed gas atmosphere comprises at least one gas selected from the group consisting of helium, argon, nitrogen, oxygen, hydrogen, carbon dioxide, and mixtures thereof; and

said thin film is from about 10 Angstroms to about 2 microns thick.

6. A method according to claim 1, wherein said separate compressed gas atmosphere comprises heated carbon dioxide at a temperature at least 5 degrees centigrade higher than the temperature of said first supercritical fluid.

7. A method according to claim 1, wherein said separate compressed gas atmosphere comprises a supercritical fluid.

8. A method for depositing a film of a material onto a surface of a substrate, said method comprising:

(a) dissolving a precursor of the material into a solvent to form a supercritical or near-supercritical solution;

(b) forming a thin film of said solution on said substrate under conditions in which said precursor is stable in said solution; and then

(c) contacting a conversion reagent to said thin film under conditions that initiate a chemical reaction involving said precursor and form a film of a chemically converted material on the surface of said substrate.

9. A method of claim 8 wherein said film forming step is carried out by (i) displacing said solution with a separate compressed gas atmosphere, (ii) lowering the density of solution so that said precursor precipitates onto said substrate, or (iii) combinations thereof.

10. A method of claim 8, wherein said contacting step is carried out with said conversion reagent in a gaseous or supercritical phase.

11. A method of claim 8, wherein said contacting step is carried out at a pressure less than ambient pressure.

12. A method of claim 8, wherein said chemical reaction produces byproducts thereof, and wherein said byproducts are removed by: (i) dissolving said byproducts in said supercritical or near-supercritical solution, (ii) dissolving said byproducts in a separate compressed gas atmosphere, or (iii) dissolving said byproducts in a subsequent fluid or compressed gas atmosphere.

13. The method of claim 8, wherein:  
said solvent comprises carbon dioxide; and  
said material comprises a metal or metallic precursor.

14. The method of claim 8, wherein said chemically converted material comprises copper.

15. The method of claim 8, wherein said substrate comprises a semiconductor having vias formed therein, and wherein said surface comprises a via wall.

16. The method of claim 15, wherein said chemically converted material comprises a barrier material deposited on said via wall.

17. The method of claim 15, wherein said chemically converted material comprises titanium nitride or tantalum nitride deposited on said via wall.

18. The method according to claim 15, wherein said chemically converted material comprises ruthenium deposited on said via wall.

19. The method of claim 16, further comprising the step of seeding said via wall with copper after said barrier material is deposited on said via wall.

20. The method of claim 16, further comprising the step of filling said via with copper subsequent to depositing said barrier material and without an intervening seeding step.

21. The method of claim 20, wherein said filling step is an electrofilling step or a carbon dioxide solvent deposition step.

22. The method of claim 8, further comprising:

(d) cyclically repeating steps (b) and (c) from 1 to 1000 times to increase the thickness of said film of material deposited on said surface.

23. A method for depositing a film of a chemically converted material onto a surface of a substrate, said method comprising:

(a) dissolving a precursor of the material into a liquid solution comprising CO<sub>2</sub>;

(b) contacting said liquid solution to said surface of said substrate under conditions in which said precursor is stable in said solution; and then

(c) contacting a reaction reagent to a surface of said substrate under conditions that initiate a chemical reaction involving said precursor and deposit a chemically converted material onto the surface of said substrate.

24. A method according to claim 23, where said chemical reaction is a reduction-oxidation (redox) reaction.

25. A method according to claim 23, where said chemical reaction is a thermally activated at the substrate surface.

26. A method according to claim 23, where said chemical reaction is a disproportionation reaction.

27. A method for depositing a film of a chemically converted material onto a surface of a substrate, said method comprising:

(a) dissolving a precursor of the material into a liquid solution comprising CO<sub>2</sub>;

(b) contacting said liquid solution to said surface of said substrate under conditions in which said precursor is stable in said solution; and then

(c) heating the substrate to convert said precursor material to form a film of a chemically converted material on said substrate.

28. A method for depositing a film of a chemically converted material onto a substrate, said method comprising:

- (a) dissolving a precursor of the material into a liquid solution comprising CO<sub>2</sub>;
- (b) forming a thin film of said solution formulation on the substrate, then
- (c) contacting a reaction reagent to said thin film under conditions that initiate a chemical reaction involving said precursor depositing a chemically converted material onto said substrate.

29. A method according to claim 28, wherein said film formation step is carried out by free meniscus coating from a composition comprising liquid CO<sub>2</sub>.

30. A methods according to claim 28, wherein said film formation step is carried out by spin coating from a composition comprising liquid CO<sub>2</sub>.

31. A method according to claim 28, wherein said film formation step is carried out by displacing said liquid solution with a supercritical fluid.

32. A method according to claim 28, wherein said film-forming step is carried out by displacing said liquid solution with a gas.